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IMPREGNATED METAL-ORGANIC FRAMEWORKS FOR THE REMOVAL OF TOXIC INDUSTRIAL CHEMICALS

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| 14. ABSTRACT Current technology-based efforts are focusing on a nanotechnology approach to sorbent development for air purification applications. Metal-organic frameworks (MOFs) are a novel class of materials that allow for specific functionalities to be designed directly into a porous framework. This report summarizes the evaluation of MOFs impregnated with various chemicals for enhanced reactivity. Specifically, MOF-5 (IRMOF-1) was impregnated with citric acid, copper acetate, copper oxide, and triethylenediamine (TEDA) and evaluated for porosity, moisture uptake, and TIC removal capabilities. Results indicate that most of the impregnated MOFs suffered substantial loss in porosity; however, some exhibited substantial chemical removal capabilities. New impregnation techniques and different impregnants will be investigated based on the results of the study. | | | | | | | | | | | | | | |
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PREFACE

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IMPREGNATED METAL-ORGANIC FRAMEWORKS FOR THE REMOVAL OF TOXIC INDUSTRIAL CHEMICALS

1. INTRODUCTION

In April 2008, Professor Omar Yaghi's group at the University of California, Los Angeles (UCLA), provided a metal organic framework (MOF), MOF-5, to the U.S. Army Edgewood Chemical Biological Center (ECBC) for impregnation and subsequent evaluation. Metal organic frameworks have the potential for incorporation into air purification technologies due to their ability to modify pore size and functionality on a molecular level. The objective of this evaluation is to assess the physical properties of selected MOFs as well as the adsorptive and reactive capabilities of impregnated MOFs to provide feedback to Prof. Yaghi's group for development of new materials. This report provides a summary of the evaluation as well as recommendations for improved MOF performance.

The development and evaluation of the MOF samples summarized in this report are part of a larger, Defense Threat Reduction Agency (DTRA) funded effort to develop novel, nanoscale porous materials for use as sorbents in air purification applications. The objective of this program is to evaluate the performance characteristics of novel sorbents versus a variety of toxic industrial chemicals (TICs) and chemical warfare agents (CWAs). Emphasis is placed on identifying/developing highly reactive materials that possess broad spectrum filtration capabilities. Successfully meeting this objective will provide users with improved/broader protection capabilities than our current filtration material, ASZM-TEDA. Alternatively, materials may complement filtration properties of ASZM-TEDA, leading to composite filters with tailorable performance. If successful, this approach will enable development of materials and filter designs to purify air via first principles.

This report is part of a series of summary reports based on the evaluation of MOF samples from UCLA. The first two reports (Peterson et al., 2008; Peterson et al., 2008) focused on IRMOF-1 (MOF-5), IRMOF-3, IRMOF-62, MOF-74, MOF-177, MOF-199, and ZIF-8 and provided recommendations for future material syntheses. The present report describes an initial effort aimed at impregnating MOFs for use in air purification applications. The results will be used to generate design rules for subsequent MOF synthesis.

2. EXPERIMENTAL PROCESS

2.1 Materials

MOF-5 (IRMOF-1) was synthesized at UCLA and subsequently sent to Guild Associates, Inc. (Dublin, Ohio) for impregnation. The structure of MOF-5 and the impregnants incorporated into MOF-5 are summarized in Figures 1 and 2.

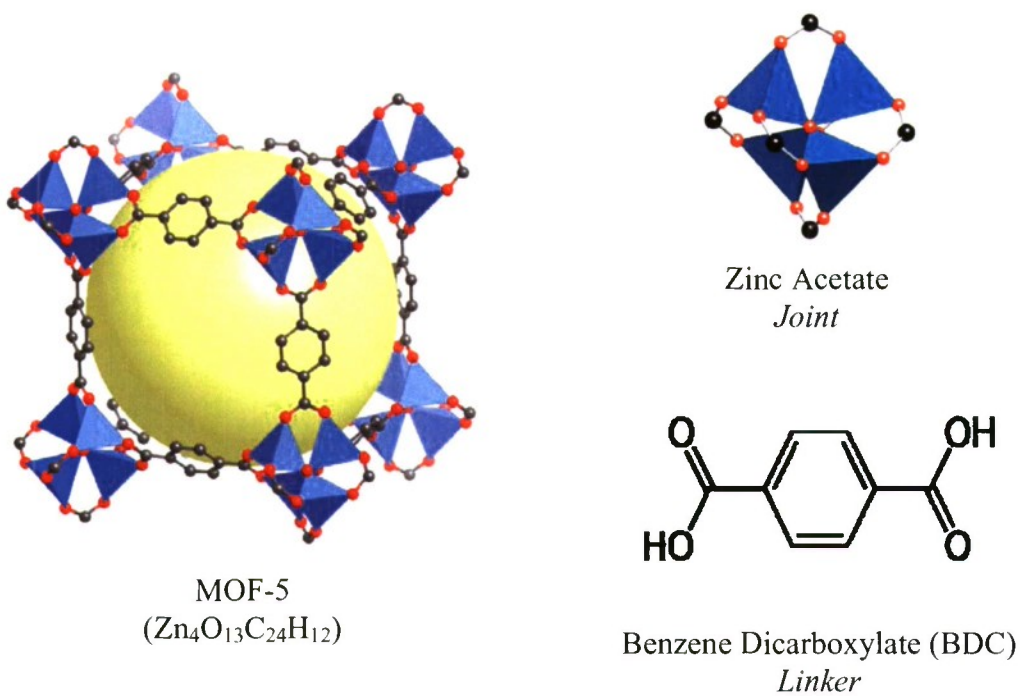
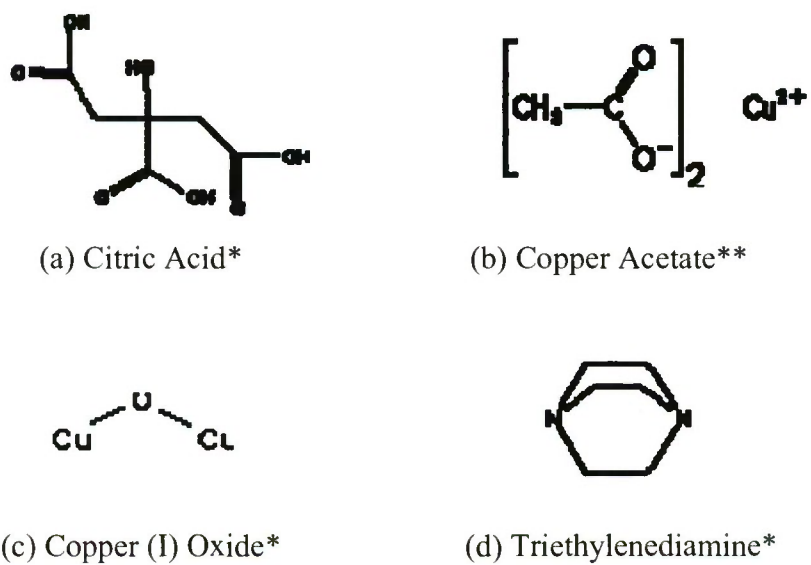


Figure 1. MOF-5 Structure



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Figure 2. Chemicals Impregnated in MOF-5

MOF-5 has the empirical formula $\text{Zn}_4\text{O}_{13}\text{C}_{24}\text{N}_3\text{H}_9$. The sample appears as “off-white” granules. MOF-5 is also known as IRMOF-1; IRMOF stands for isoreticular metal-organic framework. All IRMOFs are characterized by 6-connecting joints comprised of metal clusters, zinc acetate for the case in hand, and 2-connecting linkers (“struts”), in this case a six-member aromatic ring.

MOF-5 was impregnated with citric acid, copper acetate, copper(I) oxide, and triethylenediamine (TEDA) to enhance reactivity towards toxic chemicals. Typical impregnations of current materials, such as ASZM-TEDA, are done in an aqueous and/or ammoniacal solution. However, the structure of some MOFs have been shown to degrade in aqueous solutions and when subjected to ammonia [Peterson et al., 2008]. Therefore, work was conducted to identify suitable solvents for impregnation procedures. Solvent selection was performed by placing a small amount of MOF-5 in a vial. Various solvents were added to the vial. These solvents were n-hexane, isopropyl alcohol, acetone, water, methanol and a mixture of 20% H_2O /IPA. A photographic image of MOF-5 in the above solvents is presented below.



Figure 3. Photographic Image of MOF-5 in Selected Solvents
[N-hexane, isopropyl alcohol, acetone, water, methanol, 20%
 H_2O /IPA (L-R)]

Observations are summarized in the table below. These observations limited the choice of impregnants that could be employed. When impregnating activated carbon, basic salts of copper, zinc and molybdenum are dissolved in an ammonium hydroxide/ammonium carbonate/water solution (referred to as ammoniacal solution). Clearly, this solution would not be suitable for impregnation of MOF-5, as MOF-5 rapidly decomposes in water. As a result, the

choice of impregnants was limited to those which could be dissolved in IPA, acetone or hexane. A list of all solvents evaluated is presented in Table 1.

Table 1. Effects of Solvent Contact with MOF-5

| Solvent | Observation |
|-------------------|--|
| n-Hexane | No apparent effect |
| Isopropyl alcohol | No apparent effect |
| Acetone | No apparent effect |
| Water | Dissolves upon contact |
| Methanol | Particles turn white, break apart when vial agitated |
| 20% Water/IPA | Particles turn white, fall apart upon contact |

Citric acid was chosen as an impregnant for this study because it is known to react with ammonia. The citric acid impregnated material [MOF-5 (Ct.Ac.)] was prepared by dissolving 0.1 g citric acid in 5 ml of isopropyl alcohol. The resulting solution was used to impregnate 1 g of MOF-5. Three separate impregnations with the same solution were performed to achieve the required loading of 10 wt.%. Between impregnations, the material was dried with flowing air at room temperature. During impregnation, the material appeared soft to the touch, but hardened when dry. When soaked in IPA, even after a week, the sample was still hard. It is possible that the citric acid in solution affected the integrity of the MOF-5 structure.

Copper acetate was chosen as an impregnant for this study because it was the only copper salt that was able to dissolve into solution with the selected solvent. The copper acetate material [MOF-5 (Cu-Ac)] was prepared by adding 0.1 g copper acetate to 5 mL isopropyl alcohol in a small vial. Only a portion of the copper acetate dissolved. MOF-5 was impregnated with the solution and then IPA was added to dissolve the remaining copper acetate. This process was repeated until all of the copper acetate dissolved. This required three re-fills of the solution and about 7 impregnation steps. Between impregnations, the material was dried with flowing air at room temperature.

The copper(I) oxide sample [MOF-5 (Cu₂O)] was prepared by suspending small (less than 2 μ m) particles of copper(I) oxide in IPA, then wetting the sample with the solution. Approximately 0.1 g of copper(I) oxide and 5 mL of IPA was used for the impregnation. Copper oxide was chosen as an impregnant for this study because oxides of copper are known to react with acidic/acid-forming gases and possibly form coordination compounds with ammonia. Copper(I) oxide was chosen over copper(II) oxide to reduce the formation of cyanogen, a by-product of hydrogen cyanide (AC) reaction.

Triethylenediamine was chosen as an impregnant for this study because it is known to react with chemicals such as cyanogen chloride (CK), nitrogen dioxide, and sulfur

dioxide. The TEDA sample [MOF-5 (TEDA)] was prepared by adding 0.1 g TEDA and 1 g MOF-5 to a glass vial, and placing the vial (wrapped in tape) with the v-blender and rotating at 60 °C for 2 hr. It appears that all the TEDA was sublimed into the pores of the material. This was the only material prepared using a dry impregnation technique.

2.2 Testing Protocol

The MOFs were characterized by recording nitrogen isotherm, water adsorption equilibria, and micro-breakthrough data. Nitrogen isotherm data were obtained using a Quantachrome Autosorb Automated Gas Sorption System. Approximately 20 mg of each MOF (except the TEDA impregnated sample) were used for the analysis. Samples were outgassed at a temperature of 150 °C for at least 8 hr prior to data measurement. Nitrogen isotherm data were used to estimate the surface area, pore volume, and average pore size.

Water isotherms were collected on the MOFs and ASZM-TEDA at 25 °C. Water was delivered from a saturator cell to a temperature-controlled microbalance containing the sorbent to be evaluated. The concentration of moisture in the air, or relative humidity (RH), was systematically increased (or decreased) by changing the temperature of the saturator cell. By measuring the change in weight, the amount of water adsorbed on the material was calculated. A system schematic is illustrated in Figure 4.

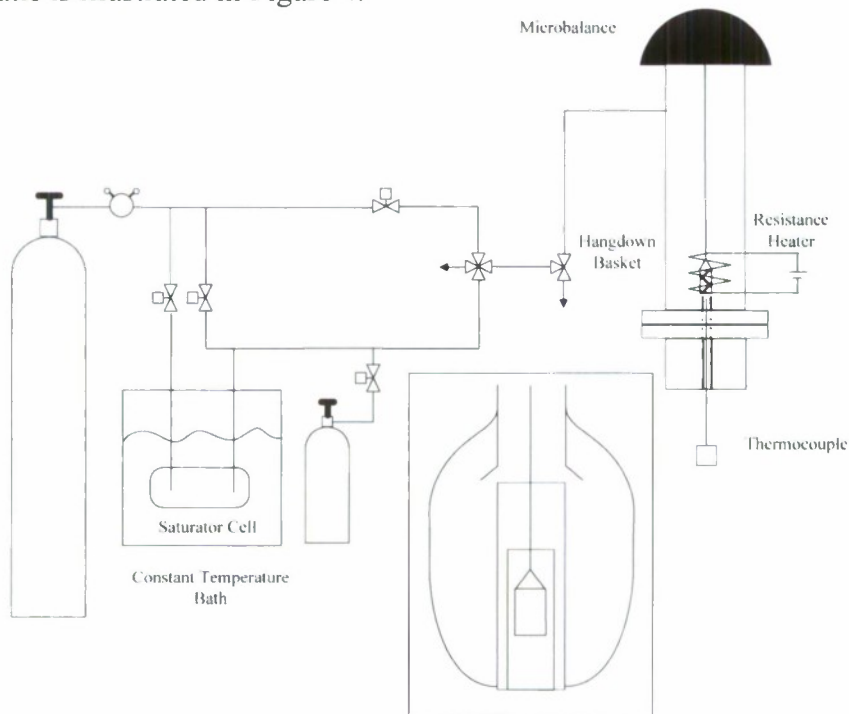


Figure 4. Water Isotherm System

Samples were evaluated for ammonia, cyanogen chloride (CK) and sulfur dioxide capacity using a micro-breakthrough system. A specific amount of chemical was injected into a ballast and subsequently pressurized. This chemical mixture was then mixed with an air stream

containing the required moisture content (from a temperature-controlled saturator cell) in order to achieve a predetermined concentration. The completely mixed stream then passed through a sorbent bed submerged in a temperature-controlled water bath. Approximately 50 mm³ of each sample were tested under dry (~0% RH) and humid (~80% RH) conditions. The effluent stream then passed through a continuously operating gas chromatograph. A system schematic is shown in Figure 5.

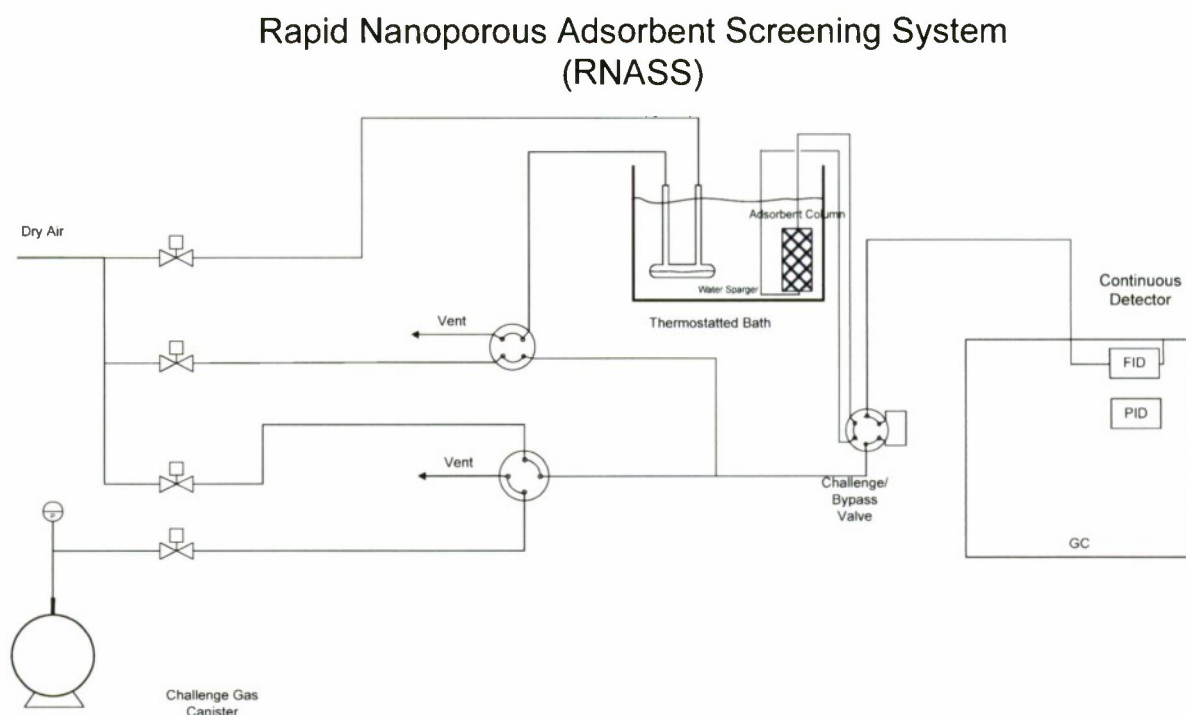


Figure 5. Rapid Nanoporous Adsorbent Screening System

Approximately 50 mm³ of sorbent were evaluated using a 1,000 mg/m³ ammonia challenge in air, a bed depth of 4 mm, a flow rate of 20 mL/min (referenced to 25 °C) through a 4 mm tube, and a RH of less than 1% (approximately -40 °C dew point). The residence time (bed volume divided by the flow rate) was approximately 0.15 s. In all cases, sorbents were pre-equilibrated for 1 hr at a RH consistent with that of the test. The effluent concentration was monitored using a photoionization detector (PID).

Approximately 50 mm³ of sorbent were evaluated using a cyanogen chloride (CIC≡N or CK) challenge at a feed concentration of 4,000 mg/m³ in air, a flow rate of 20 mL/min referenced to 25 °C, a temperature of 20 °C, and RHs of less than 1 and 80%. In all cases, sorbents were pre-equilibrated for approximately 1 hr at a RH consistent with that of the test. The effluent concentration was monitored using an HP5890 Series II Gas Chromatograph equipped with a flame ionization detector (GC/FID).

Approximately 50 mm³ of sorbent were evaluated with sulfur dioxide at a feed concentration of 1,000 mg/m³, a flow rate of 20 mL/min referenced to 25 °C, a temperature of 20 °C, and RHs of less than 1 and 80%. In all cases, sorbents were pre-equilibrated for 1 hr at a RH consistent with that of the test. The concentration eluting through the sorbent bed was monitored using an HP5890 Series II GC equipped flame photometric detector (FPD).

3. RESULTS AND DISCUSSION

3.1 Nitrogen Isotherm

Nitrogen isotherm data were collected over six orders of magnitude of relative pressure and then used to estimate the surface area, pore volume and average pore size of MOF samples. The data are illustrated in Figures 6 and 7. Table 2 summarizes the nitrogen uptake at selected relative pressures.

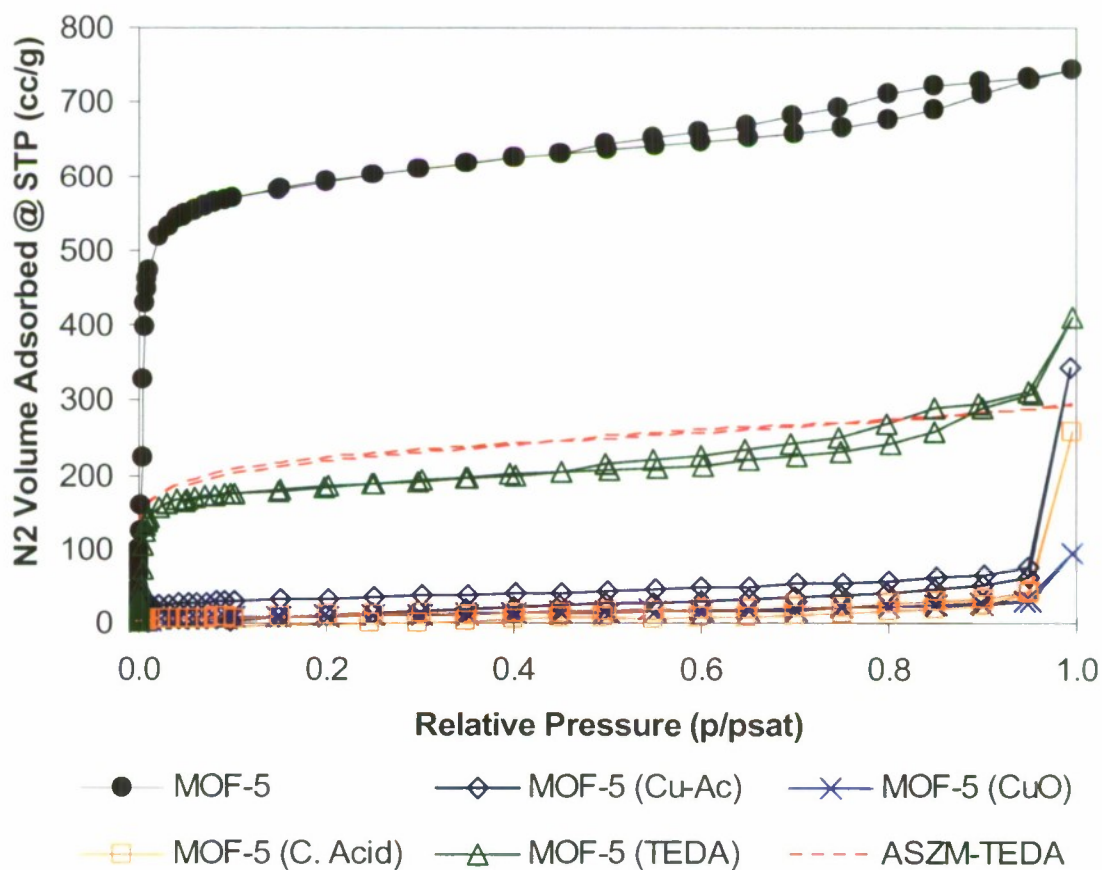


Figure 6. Nitrogen Isotherm Plot

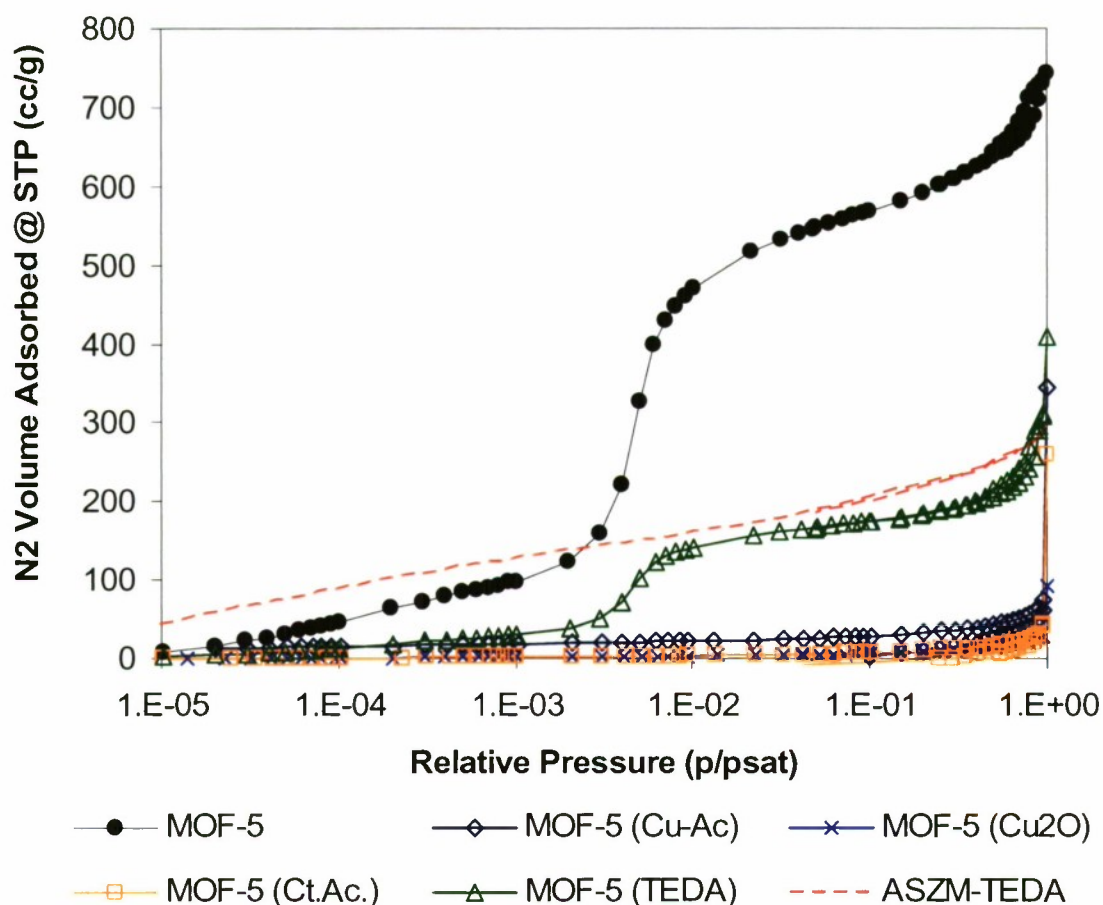


Figure 7. Nitrogen Isotherm Log Plot

All samples exhibit Type I isotherms initially; however, there is hysteresis present in most of the isotherms at higher relative pressures. Baseline MOF-5 has a much higher nitrogen uptake than ASZM-TEDA (mass basis) and all impregnated samples; however the low relative pressure uptake of nitrogen is significantly lower than that of ASZM-TEDA. All impregnated MOF-5 samples also display low nitrogen uptake at low relative pressures, indicating low adsorption potentials. For several of the impregnated samples, it is apparent that nitrogen uptake suffers over the full range of relative pressures, possibly indicating structural collapse of the materials. The only MOF-5 material that exhibits significant nitrogen adsorption is the TEDA-impregnated sample. This is the only sample that was not impregnated via wet solution. It follows that either the impregnation approach or the solvent may have contributed to destabilizing the MOF structures. Evidently, IPA was not a suitable solvent for MOF impregnation.

Table 2. Volume of Nitrogen Adsorbed on Selected Materials

| Samples | Volume N ₂ Adsorbed (cm ³ -STP/g-sorbent) | | | |
|---------------------------|---|-------------------------|------------------------|------------------------|
| | P/P ₀ = 0.001 | P/P ₀ = 0.01 | P/P ₀ = 0.1 | P/P ₀ = 0.3 |
| MOF-5 | 99 | 471 | 570 | 610 |
| MOF-5 (Cu-Ac) | 19 | 23 | 29 | 37 |
| MOF-5 (Cu ₂ O) | 2.0 | 4.0 | 6.9 | 11 |
| MOF-5 (Ct.Ac.) | 2.0 | 4.3 | 6.5 | 12 |
| MOF-5 (TEDA) | 31 | 143 | 176 | 193 |
| ASZM-TEDA | 128 | 161 | 205 | 233 |

From the nitrogen isotherm plots, values were calculated for $1/[W((P_0/P)-1)]$ and plotted against relative pressure to calculate BET capacity. Values for this calculation are summarized in Table 3.

Table 3. Fit Parameters for Calculated BET

| Sample | Slope | Y-Intercept | R ² | C |
|---------------------------|-------|-------------|----------------|-------|
| MOF-5 | 1.483 | 0.002368 | 0.999968 | 627.1 |
| MOF-5 (Cu-Ac) | 29.39 | 0.1035 | 0.999986 | 284.9 |
| MOF-5 (Cu ₂ O) | 107.9 | 2.209 | 0.999958 | 49.85 |
| MOF-5 (Ct.Ac.) | 113.1 | 1.269 | 0.998901 | 90.10 |
| MOF-5 (TEDA) | 4.869 | 0.008012 | 0.999985 | 608.7 |
| ASZM-TEDA | 4.224 | 0.0104300 | 0.999971 | 406.1 |

Nitrogen isotherm data were used to calculate the BET capacity and total pore volume. The term BET capacity, not surface area, is used for reasons described in Walton and Snurr (2007) and Rouquerol et al. (2007). Table 4 summarizes the calculated values.

Table 4. Calculated BET Capacity and Porosity of MOFs

| Sample | BET Capacity (m ² /g) | Pore Volume (cc/g) |
|---------------------------|----------------------------------|--------------------|
| MOF-5 | 2,345 | 1.15 |
| MOF-5 (Cu-Ac) | 181 | 0.54 |
| MOF-5 (Cu ₂ O) | 32 | 0.14 |
| MOF-5 (Ct.Ac.) | 30 | 0.40 |
| MOF-5 (TEDA) | 714 | 0.64 |
| ASZM-TEDA | 820 | 0.46 |

Impregnation of MOF-5 with TEDA reduced the BET capacity, likely due to the presence of TEDA within the pores of the structure, and not due to a structural destabilization. It is apparent from the data summarized in Table 3 that impregnating MOF-5 with the IPA solution is extremely detrimental to the calculated BET capacity. In addition, the pore volume decreases significantly for all samples as compared to the baseline MOF-5. For those impregnated from solution, this further demonstrates the collapse of the structure. However, most structures still exhibit extensive porosity, likely located in the macroporous region and comprised of large voids. To determine the type and amount of pores in the structures, density functional theory (DFT) cumulative pore volumes were plotted as shown in Figure 8.

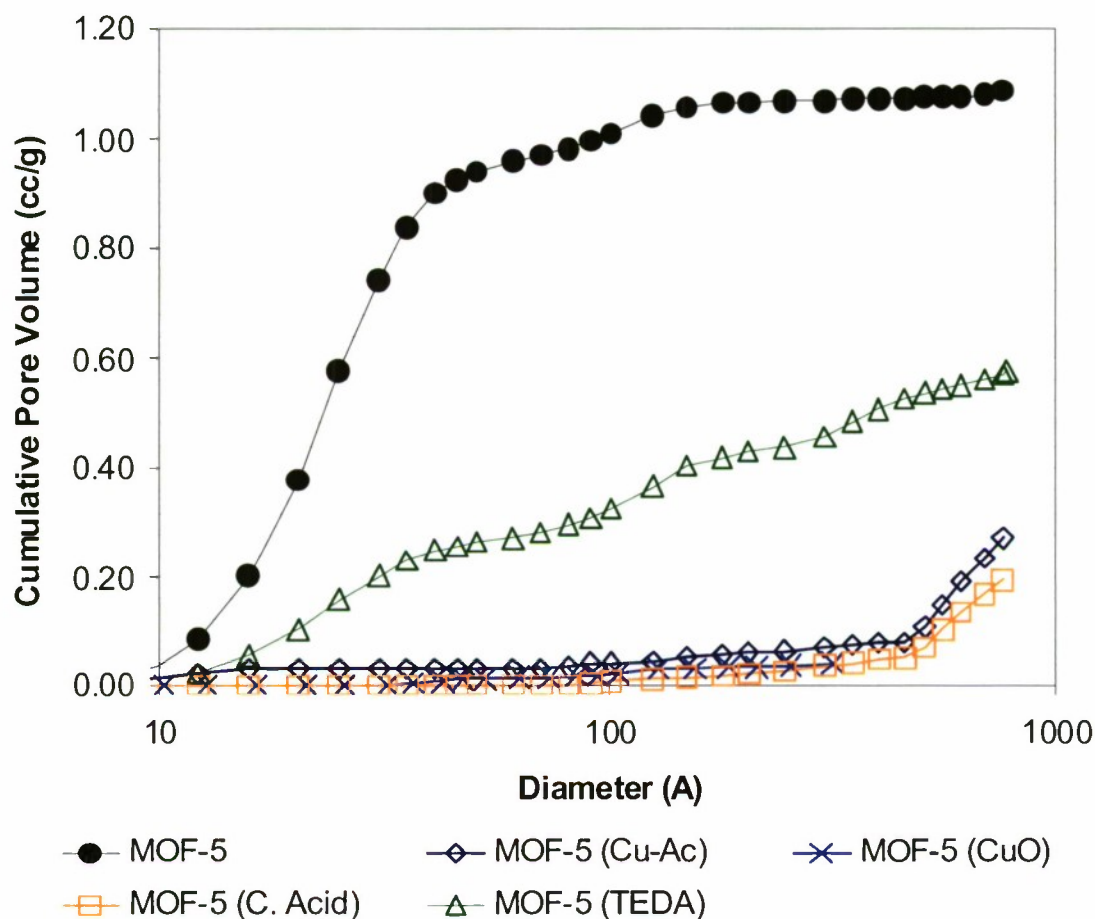


Figure 8. DFT Cumulative Pore Volume

Figure 8 illustrates that the MOFs impregnated from solution, namely the copper acetate, Copper(I) oxide, and citric acid materials, all exhibit essentially no volume of nitrogen adsorbed in the micropore region (less than 20 Å or 2 nm) or the mesopore region (20-500 Å or 2-50 nm). Only for pores greater than 50 nm does nitrogen begin to appreciably adsorb, indicating extensive macroporosity. The MOF-5 sample exhibits extensive microporosity and mesoporosity, and the TEDA-impregnated sample has a wide range of micropores, mesopores and macropores, likely because the TEDA impregnation did not collapse the structure.

Water AE were collected on MOF samples using a Cahn balance to assess the moisture uptake at a full range of RH conditions. These data will be used to determine if the samples will preferentially adsorb water as opposed to toxic chemicals. AE data for MOF and baseline samples are shown in Figure 9.

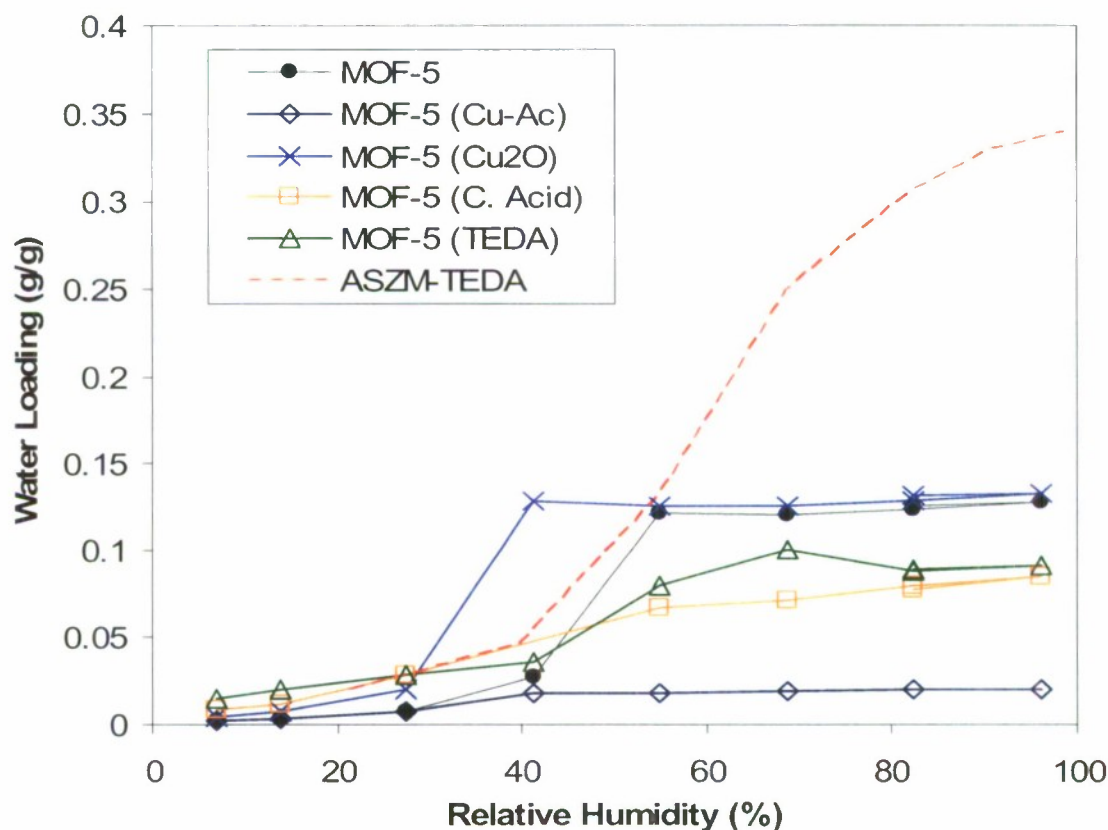


Figure 9. Water AE at 25 °C

All MOF samples generally adsorb less moisture than ASZM-TEDA, especially at high RH conditions. The MOF-5 (Cu-Ac) adsorbs the least moisture over the entire range of RHs. One reason for this is that the MOF structure has likely collapsed. Based on nitrogen isotherm results, this behavior would be expected for the samples impregnated with citric acid and copper(I) oxide; however, both exhibit higher moisture pickup than the copper acetate impregnated material. The solubility of citric acid in water helps explain why the material picks up moisture. The copper(I) oxide material, however, is insoluble in water; the reason for the high moisture pickup is unknown. Moisture uptakes are summarized in Table 5.

Table 5. Moisture Loading of Sorbents at 25 °C

| Sample | Water Loading (g-water/g-sorbent) | | |
|---------------------------|-----------------------------------|--------|--------|
| | 15% RH | 50% RH | 80% RH |
| MOF-5 | 0.003 | 0.088 | 0.123 |
| MOF-5 (Cu-Ac) | 0.003 | 0.018 | 0.019 |
| MOF-5 (Cu ₂ O) | 0.008 | 0.126 | 0.128 |
| MOF-5 (Ct.Ac.) | 0.013 | 0.061 | 0.078 |
| MOF-5 (TEDA) | 0.021 | 0.064 | 0.090 |
| ASZM-TEDA | 0.015 | 0.088 | 0.279 |

In general, moisture loadings of the MOF samples are lower than ASZM-TEDA, especially at high RH conditions. One possible explanation for the lower moisture uptake is the structural collapse under humid conditions. As noted previously, MOF-5 rapidly decomposes in water. The extent of this collapse was quantified by recording nitrogen isotherms on MOF-5 prior to and following exposure to 80% RH air for 120 min. Figure 10 illustrates the results.

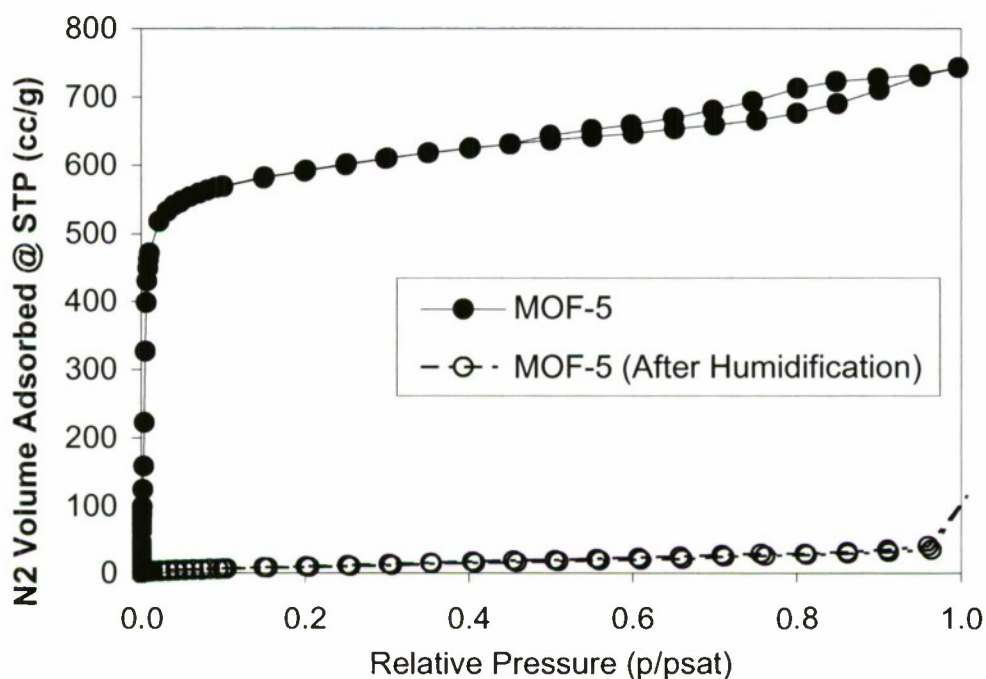


Figure 10. Nitrogen Isotherm Data before and after Exposure to High RH

Data reported in Figure 10 indicate that almost no nitrogen adsorbs on MOF-5 after it is humidified for 2 hr at 80% RH. This result clearly demonstrates that the structural integrity of MOF-5 has been severely compromised via exposure to humid air.

Ammonia micro-breakthrough testing was conducted employing MOF samples under dry and humid conditions in order to assess ammonia reactive capacity and, more generally, the removal capacity of MOFs for basic gases. ASZM-TEDA was run as a baseline sample and is known to have a limited ammonia removal capacity, especially under conditions of low RH. Approximately 50 mm³ of sorbent were tested at a feed concentration of 1,000 mg/m³ in air, a flow rate of 20 mL/min (referenced to 25 °C) through a 4-mm tube, and RH conditions of approximately 0 and 80%. In all cases, sorbents were pre-equilibrated for at least 1 hr at the same RH as the test. The feed and effluent concentrations were monitored with a PID. Ammonia breakthrough curves recorded under dry RH conditions are illustrated in Figure 11.

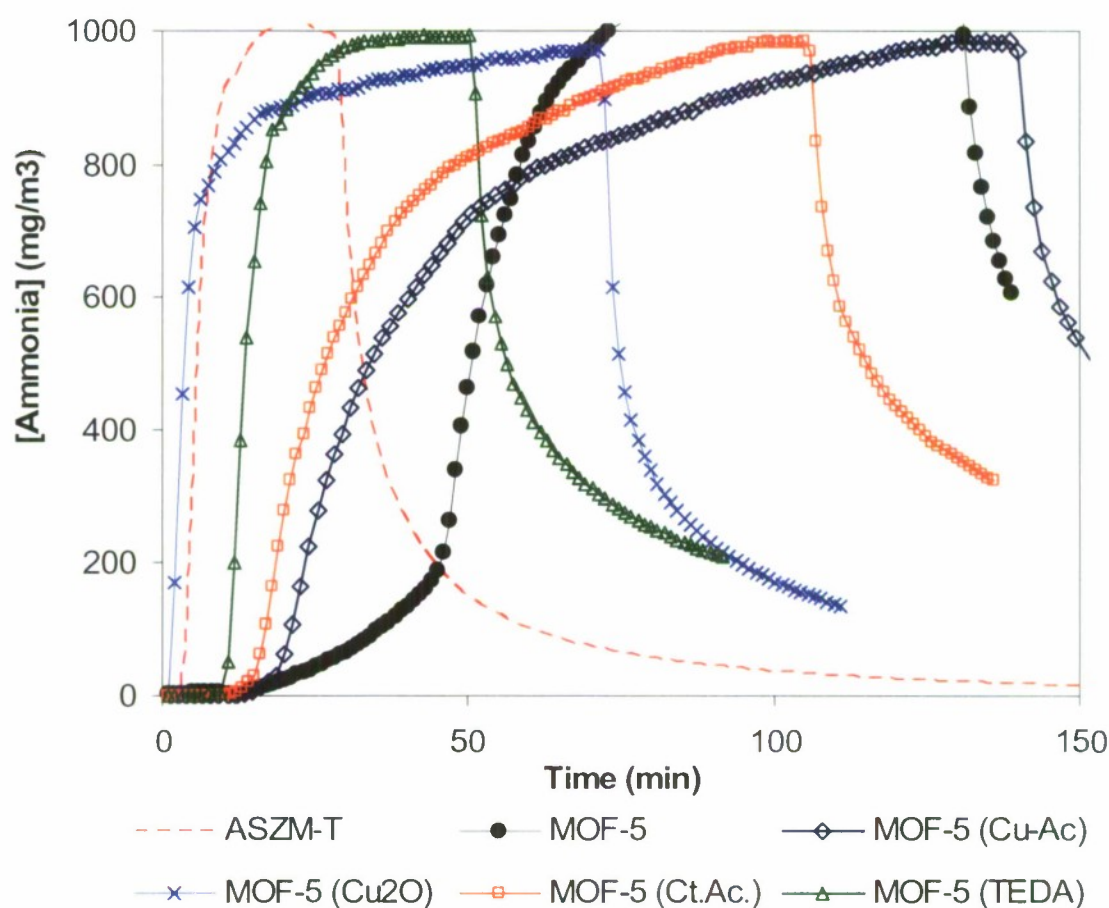


Figure 11. Ammonia Breakthrough Curves under Dry (RH = 0%) Conditions
[Ammonia] ~1000 mg/m³

As summarized in Figure 11, several of the MOFs exhibit significantly improved ammonia filtration than ASZM-TEDA. In particular, MOF-5, MOF-5 (Cu-Ac), and MOF-5 (Ct.Ac.) display the best filtration capabilities on a volume basis. In all cases, ammonia removal

is governed by either weak physical adsorption or weak chemical reaction, as evidenced by the desorption curves. Upon discontinuation of the feed, NH_3 continues to elute from the sample. The baseline MOF-5 sample provides the most extensive ammonia removal; due to the lack of functional groups on this material, the reason for this is unclear. One possibility is the presence of dimethylformamide (DMF) from synthesis which may provide hydrogen bonding sites for ammonia.* Although there is a lack of microporosity in many of the impregnated materials, ammonia appears to be removed. In the copper acetate impregnated material, ammonia likely coordinates weakly with the copper atom or acetate ligand. Alternatively, ammonium salt results from a reaction with citric acid. The TEDA impregnant may also hydrogen bond with ammonia, although this interaction is very weak as both chemicals are basic. In all cases, extensive initial ammonia capacity is provided; however, significant desorption occurs.

Ammonia breakthrough curves under humid (80% RH) conditions are illustrated in Figure 12.

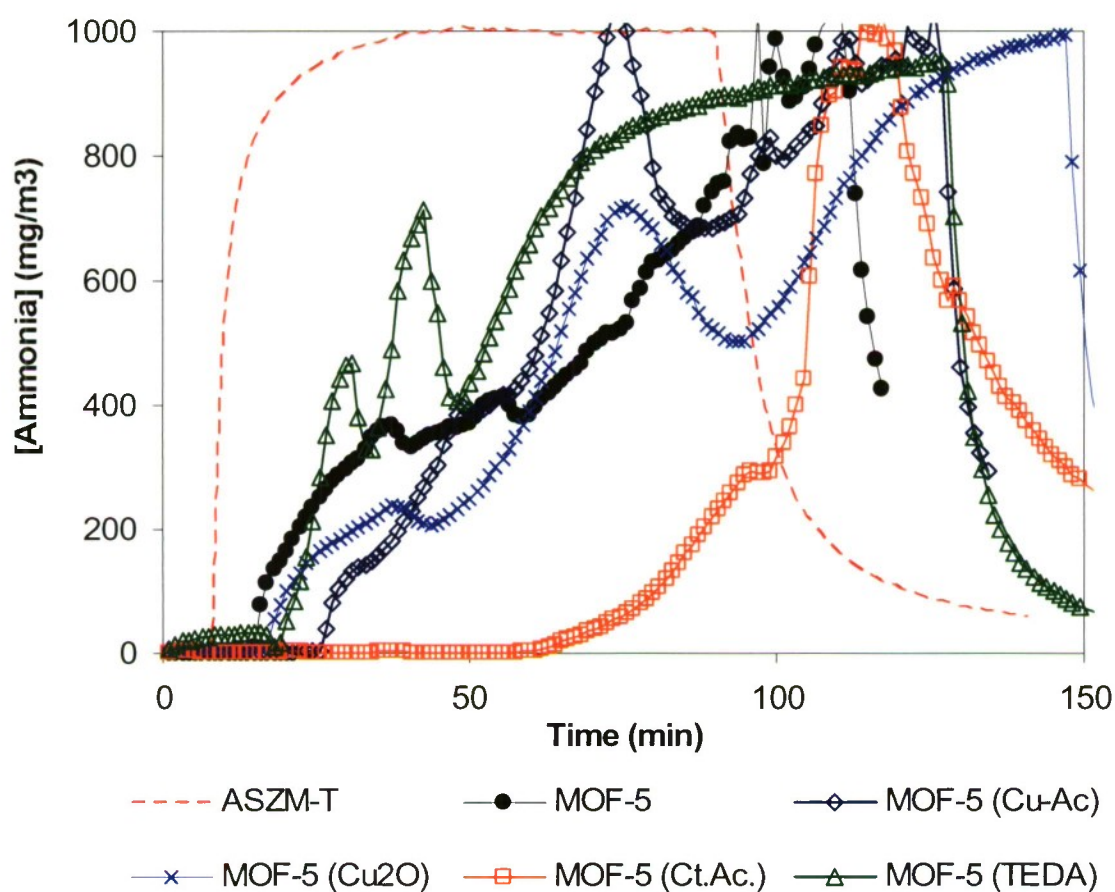


Figure 12. Ammonia Breakthrough Curves under Humid (RH = 80%) Conditions
[Ammonia] $\sim 1,000 \text{ mg/m}^3$

* George Wagner, U.S. Army Edgewood Chemical Biological Center. Unpublished Data, April 2008.

Unlike the ammonia data under low RH conditions, the high RH data are highly variable, following the trends in previous studies (Peterson et al., 2008). One possible cause is the initial adsorption of ammonia followed by periodic expulsion of ammonia and water from the MOF. Essentially, ammonia adsorbs onto the sample. As moisture degrades the structure, ammonia is released. Furthermore, this variance of water concentration causes the photoionization detector to quench, leading to inconsistent output. On a volume basis, all materials have longer breakthrough times than ASZM-TEDA. In particular, the citric acid impregnated provides excellent removal of ammonia; previous data on citric acid impregnated H-ZSM-5 confirms this trend.[†] The likely removal mechanism is an initial acid-base reaction to form the ammonium citrate followed by physical adsorption and solution effects. Copper impregnated materials may also provide coordination reactions with ammonia, and ammonia may hydrogen bond with the TEDA impregnant.

Ammonia breakthrough data were used to calculate the loading at saturation and the loading accounting for desorption; the results are summarized in Table 6.

Table 6. Ammonia Dynamic Capacity of Sorbents

| Sample | Sorbent Mass (mg) | Loading @ Full Saturation (mol/kg) | Loading After Desorption (mol/kg) |
|----------------------------------|-------------------|------------------------------------|-----------------------------------|
| MOF-5, dry | 14.8 | 3.44 | 2.87** |
| MOF-5, humid | 12.3 | 6.03 | 5.64** |
| MOF-5 (Cu-Ac), dry | 15.8 | 3.35 | 1.92 |
| MOF-5 (Cu-Ac), humid | 12.3 | 7.80 | 7.09 |
| MOF-5 (Cu ₂ O), dry | 9.7 | 1.11 | 0.00 |
| MOF-5 (Cu ₂ O), humid | 14.5 | 6.02 | 4.69 |
| MOF-5 (Ct.Ac.), dry | 21.2 | 2.09 | 0.97** |
| MOF-5 (Ct.Ac.), humid | 16.5 | 7.07 | 5.67 |
| MOF-5 (TEDA), dry | 14.4 | 1.24 | 0.05 |
| MOF-5 (TEDA), humid | 22.5 | 2.61 | 2.20 |
| ASZM-TEDA (Dry) | 14.1 | 0.54 | 0.00 |
| ASZM-TEDA (Wet) | 8.7 | 1.30 | 0.00 |

*Dry basis – does not include mass of loaded water.

**Material was still desorbing when test was terminated.

3.4 CK Micro-Breakthrough

Cyanogen Chloride micro-breakthrough testing was conducted on MOF samples under dry and humid conditions to assess CK reactive capacity. In addition to information on CK removal capabilities, breakthrough curves may also indicate the ability of MOFs to remove acid gases, as HCl is a known hydrolysis product of CK. ASZM-TEDA was evaluated as a baseline sample and has a relatively high CK removal capacity. Approximately 50 mm³ of sorbent were tested at a feed concentration of 4,000 mg/m³, a flow rate of 20 mL/min referenced

[†] Peterson and Rossin, U.S. Army Edgewood Chemical Biological Center. Unpublished Data, 2006.

to 25 °C, a temperature of 20 °C, and RHs of less than 1 and 80%. In all cases, sorbents were pre-equilibrated for approximately 1 hr at an RH consistent with that of the test. When testing at 80% RH, it is likely that a significant portion of the structure of the unimpregnated MOF-5 has been compromised. The feed and effluent concentrations were monitored using an HP5890 Series II GC/FID. CK breakthrough curves for MOF and baseline samples under low-RH conditions are illustrated in Figure 13.

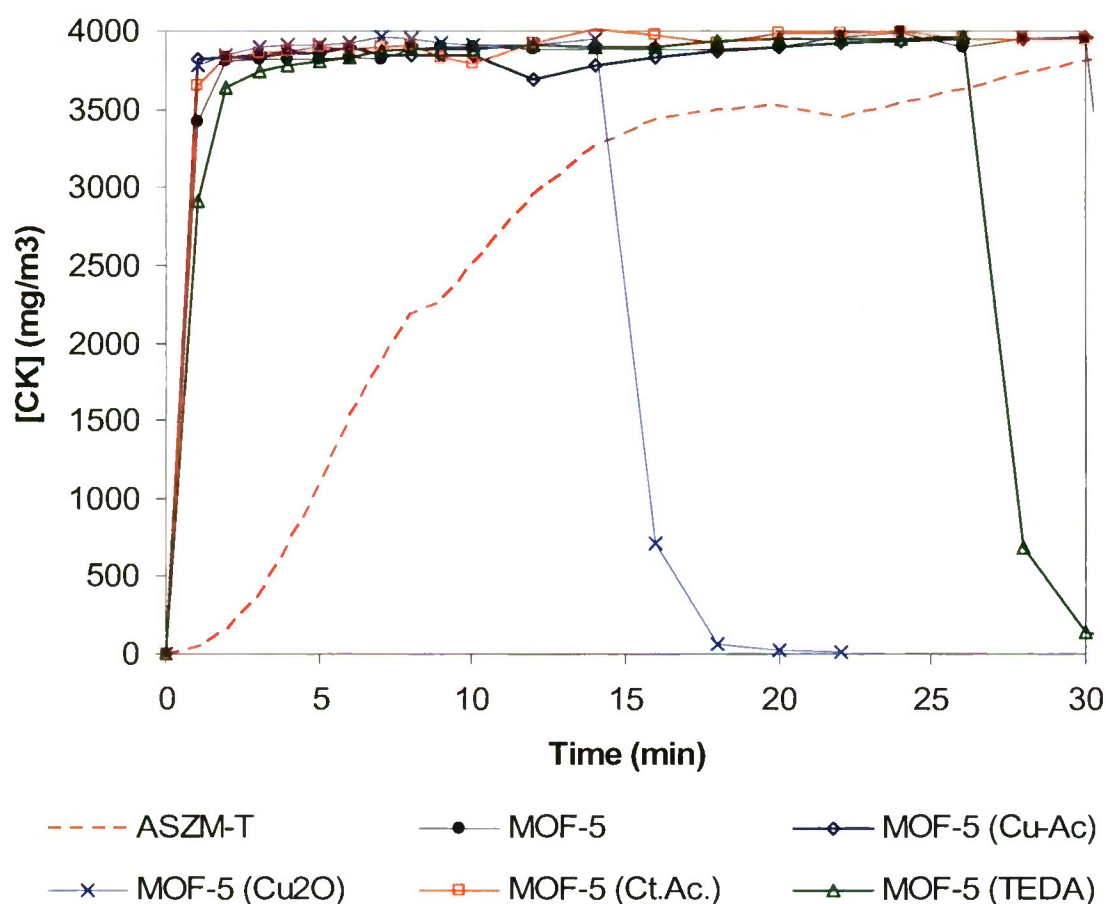


Figure 13. CK Breakthrough Curves Recorded under Low-RH Conditions
[CK Challenge] = 4,000 mg/m³

ASZM-TEDA exhibits some uptake of CK under low RH conditions; however, CK breaks through all other materials instantaneously, achieving the challenge concentration in less than 1 min. It was expected that at least some of the impregnated MOFs would exhibit CK removal capacity, due to reactions involving CK and metals. However, removal mechanisms involving CK are complicated (Zabor 1946), and it is possible that the lack of micropore volume minimizes retention, providing insufficient contact time for the reaction to complete.

Breakthrough curves for MOF and baseline samples collected under humid (80% RH) conditions are illustrated in Figure 14.

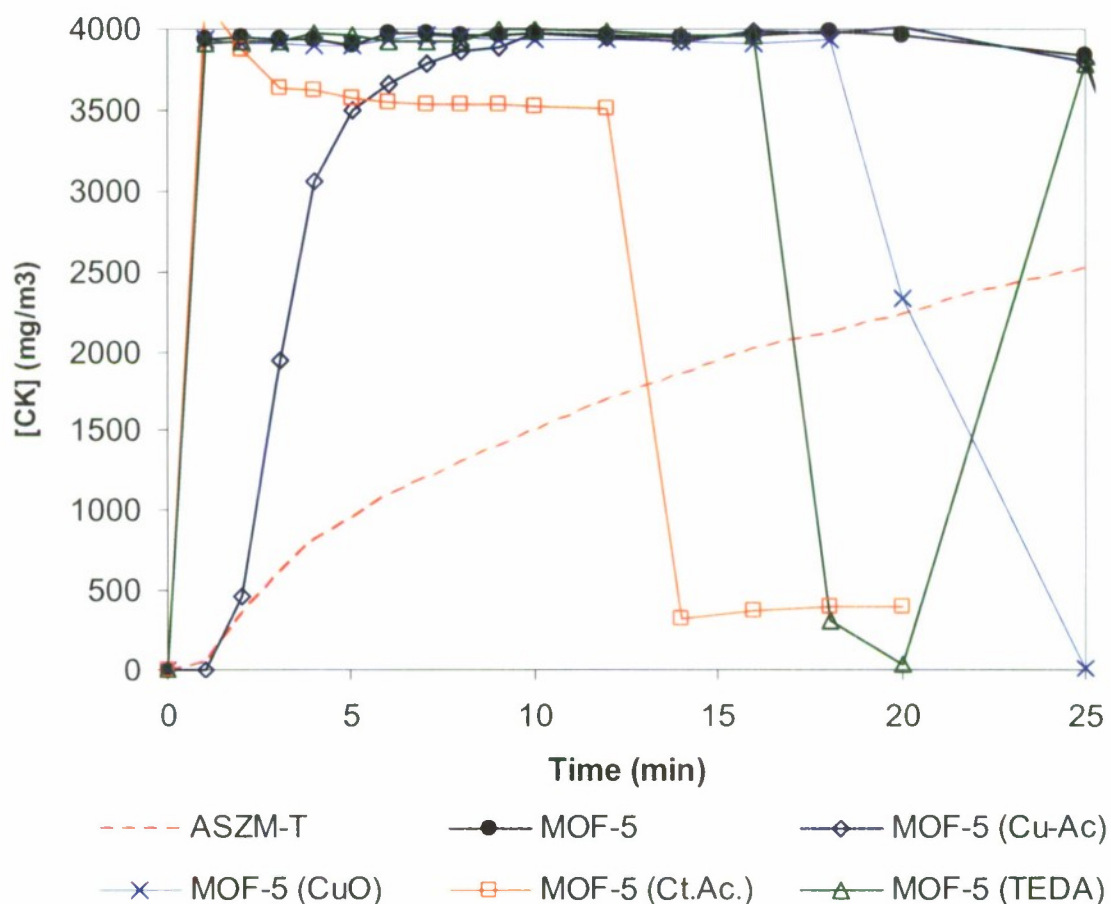


Figure 14. CK Breakthrough Curves under Humid (RH = 80%) Conditions
[CK Challenge] = 4,000 mg/m³

As with the dry conditions, ASZM-TEDA is the only sorbent studied that exhibits extensive CK removal capacity. Surprisingly, the TEDA impregnated sample displayed no CK removal capacity. One possible explanation is that moisture lead to collapse of the structure, preventing access of CK to the TEDA trapped within. Also surprising was that the copper acetate impregnated material displayed some CK removal capabilities, but to a much lesser extent than ASZM-TEDA. Reactions between CK and metal acetates have not been reported. One possible removal mechanism is the slight hydrolysis of CK, creating hydrogen chloride, which subsequently reacts with the copper impregnant.

CK breakthrough data were used to calculate the dynamic capacity of the sorbents to the stoichiometric center using the same methodology used for ammonia. The results are summarized in Table 7.

Table 7. CK Dynamic Capacity of Sorbents

| Sample | Sorbent Mass (mg) | Loading @ Full Saturation (mol/kg) | Loading After Desorption (mol/kg) |
|----------------------------------|-------------------|------------------------------------|-----------------------------------|
| MOF-5, dry | 10.5 | 0.19 | 0.07 |
| MOF-5, humid | 15.9 | 0.04 | 0.00 |
| MOF-5 (Cu-Ac), dry | 13.4 | 0.43 | 0.02 |
| MOF-5 (Cu-Ac), humid | 11.1 | 0.05 | 0.02 |
| MOF-5 (Cu ₂ O), dry | 12.8 | 0.07 | 0.05 |
| MOF-5 (Cu ₂ O), humid | 10.7 | 0.07 | 0.03 |
| MOF-5 (Ct.Ac.), dry | 9.9 | 0.14 | 0.08 |
| MOF-5 (Ct.Ac.), humid | 21.4 | 0.09 | 0.02 |
| MOF-5 (TEDA), dry | 12.9 | 0.15 | 0.07 |
| MOF-5 (TEDA), humid | 13.0 | 0.05 | 0.01 |
| ASZM-TEDA (Dry) | 5.8 | 2.49 | 2.00 |
| ASZM-TEDA (Wet) | 11.8 | 3.12 | 3.03 |

*Dry basis – does not include mass of loaded water.

3.5 Sulfur Dioxide Micro-Breakthrough

Sulfur dioxide micro-breakthrough testing was conducted on MOF samples under dry and humid test conditions in order to assess sulfur dioxide reactive capacity, and, more generally, the removal capacity of MOF samples for weak acid gases. The assumption is that if MOFs show removal mechanisms for weakly acidic gases, then strong acids should also be removed. ASZM-TEDA was tested as a baseline sample and has a relatively high sulfur dioxide removal capacity. Approximately 50 mm³ of sorbent were tested at a feed concentration of 1,000 mg/m³, a flow rate of 20 mL/min referenced to 760 Torr and 25 °C, a temperature of 20 °C, and RHs of less than 1 and 80%. In all cases, sorbents were pre-equilibrated for 1 hr at the same RH as the test. The concentration eluting through the sorbent was monitored with an FPD. Sulfur dioxide breakthrough curves for MOF and baseline samples are illustrated in Figures 15 and 16.

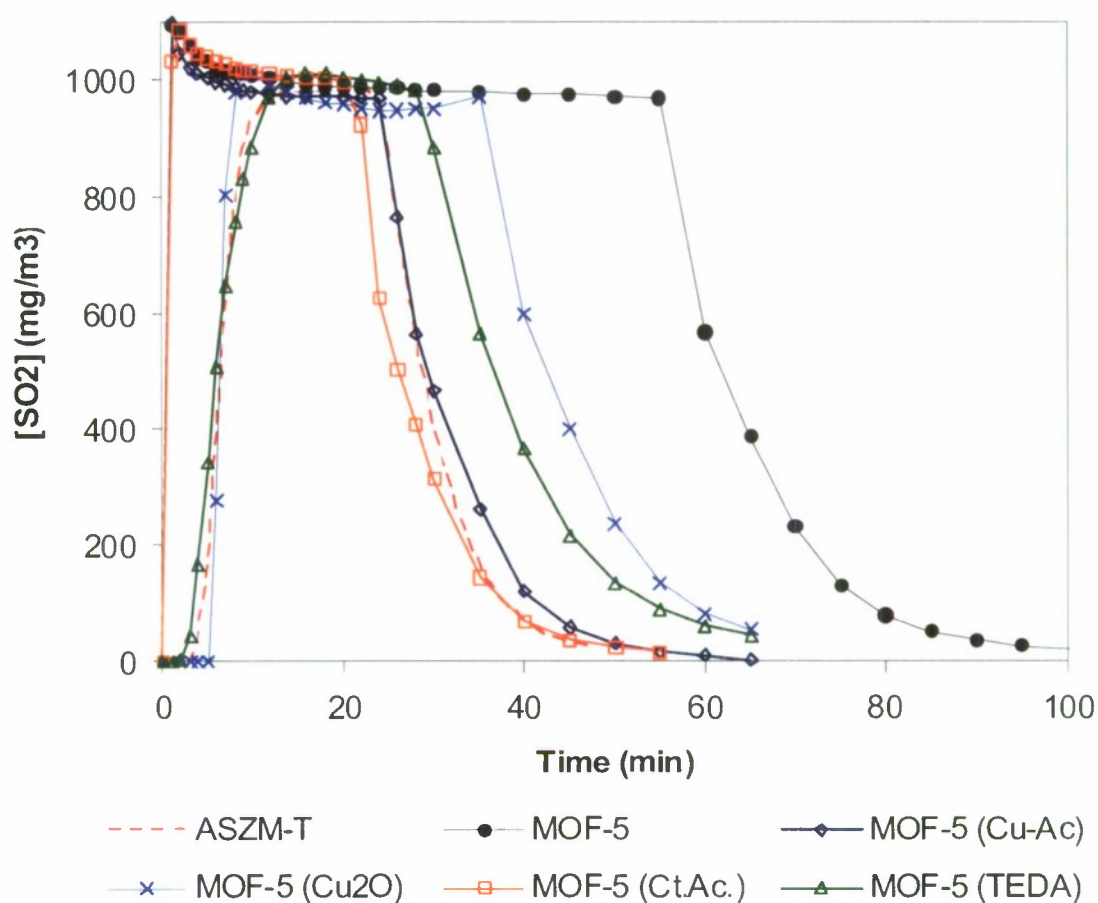


Figure 15. SO₂ Breakthrough Curves Recorded under Dry (RH < 1%) Test Conditions
[Challenge] = 1,000 mg/m³

On a volume basis, ASZM-TEDA and the MOFs impregnated with copper(I) oxide and TEDA exhibit similar SO₂ removal capabilities, however ASZM-TEDA has a higher capacity on a mass basis. Sulfur dioxide is known to react with TEDA,^{*} and it may be possible for a reaction with the copper(I) oxide impregnant as well to form a copper sulfite or copper(I) sulfide.

Figure 16 shows SO₂ breakthrough curves recorded under high RH conditions.

^{*} Peterson, U.S. Army Edgewood Chemical Biological Center. Unpublished Data, 2007.

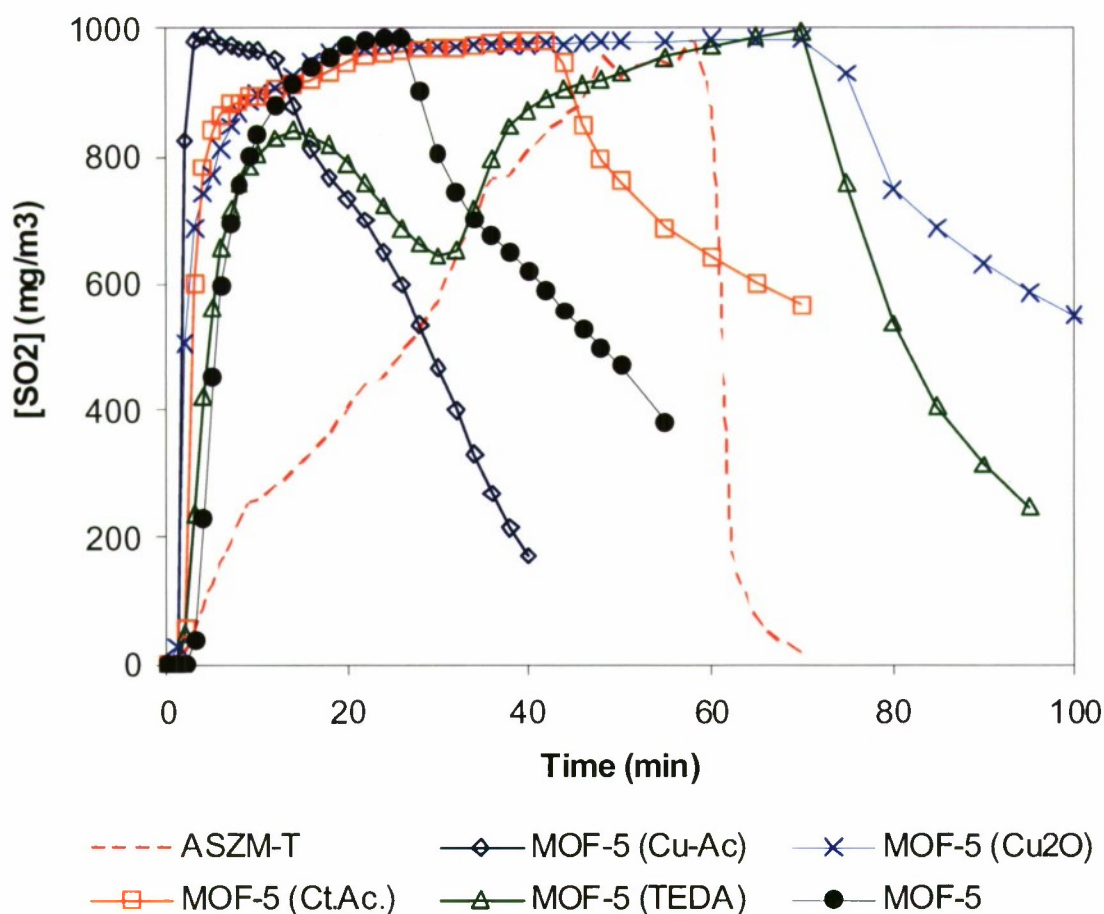


Figure 16. SO₂ Breakthrough Curves under Humid (RH = 80%) Conditions
[Challenge] = 1,000 mg/m³

Under high RH conditions, ASZM-TEDA provides substantial SO₂ removal through reactions with impregnants. Sulfur dioxide breaks through the MOFs studied almost immediately, although the top ends of the breakthrough curves indicate some reaction is taking place. Again, the lack of SO₂ removal capacity associated with the MOF samples is attributed to a structural collapse brought about by the humid exposure. Sulfur dioxide likely reacts with the TEDA impregnant; however, small quantities of SO₂ are removed in other MOFs through solubility effects with adsorbed moisture. In all MOFs, any SO₂ initially removed desorbs from the sample after feed termination.

Breakthrough data on SO₂ were used to calculate the dynamic capacity using the same methodology as was used for ammonia. The results are summarized in Table 8.

Table 8. SO₂ Dynamic Capacity of Sorbents

| Sample | Sorbent Mass (mg) | Loading @ Full Saturation (mol/kg) | Loading After Desorption (mol/kg) |
|----------------------------------|-------------------|------------------------------------|-----------------------------------|
| MOF-5, dry | 17.7 | 0.02 | 0.00 |
| MOF-5, humid | 20.8 | 0.10 | 0.00 |
| MOF-5 (Cu-Ac), dry | 17.7 | 0.01 | 0.00 |
| MOF-5 (Cu-Ac), humid | 24.3 | 0.03 | 0.00 |
| MOF-5 (Cu ₂ O), dry | 25.7 | 0.09 | 0.00 |
| MOF-5 (Cu ₂ O), humid | 14.4 | 0.11 | 0.00 |
| MOF-5 (Ct.Ac.), dry | 37.7 | 0.00 | 0.00 |
| MOF-5 (Ct.Ac.), humid | 37.1 | 0.04 | 0.00 |
| MOF-5 (TEDA), dry | 31.8 | 0.01 | 0.00 |
| MOF-5 (TEDA), humid | 12.3 | 0.36 | 0.08 |
| ASZM-TEDA (Dry) | 5.2 | 0.42 | 0.07 |
| ASZM-TEDA (Wet) | 5.0 | 1.60 | 1.51 |

*Dry basis – does not include mass of loaded water.

4. SUMMARY

MOF-5 (IRMOF-1) was impregnated with citric acid, copper acetate, copper oxide, and triethylenediamine (TEDA) and evaluated for porosity, moisture uptake, and TIC removal capabilities. A decrease in porosity was also observed for the TEDA impregnated sample, and is attributed to the presence of TEDA within the pores. Results indicate that MOF-5 impregnated using IPA solutions suffered substantial loss in porosity, however, some exhibited substantial chemical removal capabilities. Tables 9 and 10 summarize the MOFs evaluated, porosity measurements, and chemical removal capabilities at saturation, and Figure 17 illustrates the chemical removal capacities of the sorbents evaluated.

Table 9. Comparison of Physical Properties of Sorbents Studied

| Sample | Impregnant | BET Capacity | Pore Volume | H ₂ O Capacity @ 80% RH |
|---------------------------|------------------|--------------|-------------|------------------------------------|
| | | m^2/g | g/cc | g/g |
| MOF-5 | None | 2,345 | 1.15 | 0.123 |
| MOF-5 (Cu-Ac) | Copper acetate | 181 | 0.54 | 0.019 |
| MOF-5 (Cu ₂ O) | Copper(I) oxide | 32 | 0.14 | 0.128 |
| MOF-5 (Ct.Ac.) | Citric acid | 30 | 0.40 | 0.078 |
| MOF-5 (TEDA) | TEDA | 714 | 0.64 | 0.090 |
| ASZM-T | Activated carbon | 820 | 0.46 | 0.279 |

Table 10. Comparison of Chemical Removal Properties of Sorbents Studied

| Sample | Impregnant | RH | NH ₃ Capacity | CK Capacity | SO ₂ Capacity |
|---------------------------|------------------|-----|-----------------------------|----------------|-----------------------------|
| | | | <i>mol/kg</i> | <i>mol/kg</i> | <i>mol/kg</i> |
| MOF-5 | None | Dry | 3.40 | 0.19 | 0.02 |
| | | Wet | 5.87 | 0.04 | 0.10 |
| | | | | | |
| MOF-5 (Cu-Ac) | Copper acetate | Dry | 3.35 | 0.05 | 0.01 |
| | | Wet | 7.80 | 0.43 | 0.03 |
| | | | | | |
| MOF-5 (Cu ₂ O) | Copper oxide | Dry | 1.11 | 0.07 | 0.09 |
| | | Wet | 6.02 | 0.07 | 0.11 |
| | | | | | |
| MOF-5 (Ct.Ac.) | Citric acid | Dry | 2.09 | 0.14 | 0.00 |
| | | Wet | 7.07 | 0.09 | 0.04 |
| | | | | | |
| MOF-5 (TEDA) | TEDA | Dry | 1.24 | 0.15 | 0.01 |
| | | Wet | 2.61 | 0.05 | 0.36 |
| | | | | | |
| ASZM-T (Dry) | Activated carbon | Dry | 0.54 | 2.49 | 0.42 |
| | | Wet | 1.30 | 3.12 | 1.10 |

One major finding associated with this study is that MOF-5 is unstable under humid conditions. A second major finding of this study is that the wet impregnation technique used to impregnate the MOFs was unsuccessful, as it led to the destruction of the microstructure and the reduction in BET capacity and pore volume. With only macropores available in most of the impregnated materials, extensive chemical reaction could not take place for either CK or sulfur dioxide; however, all materials performed well against ammonia. Although the current effort did not lead to a material with a solid structure and extensive chemical removal properties, it may be possible to attempt impregnation with other solvents that are more compatible with MOFs, such as dimethylformamide (DMF), chloroform, and methylene chloride, all of which are used in MOF synthesis. In addition, it may be possible to impregnate MOFs via vapor deposition techniques. Based on the breakthrough data collected, however, it seems prudent to point future efforts towards a material that is more stable in a high humidity environment.

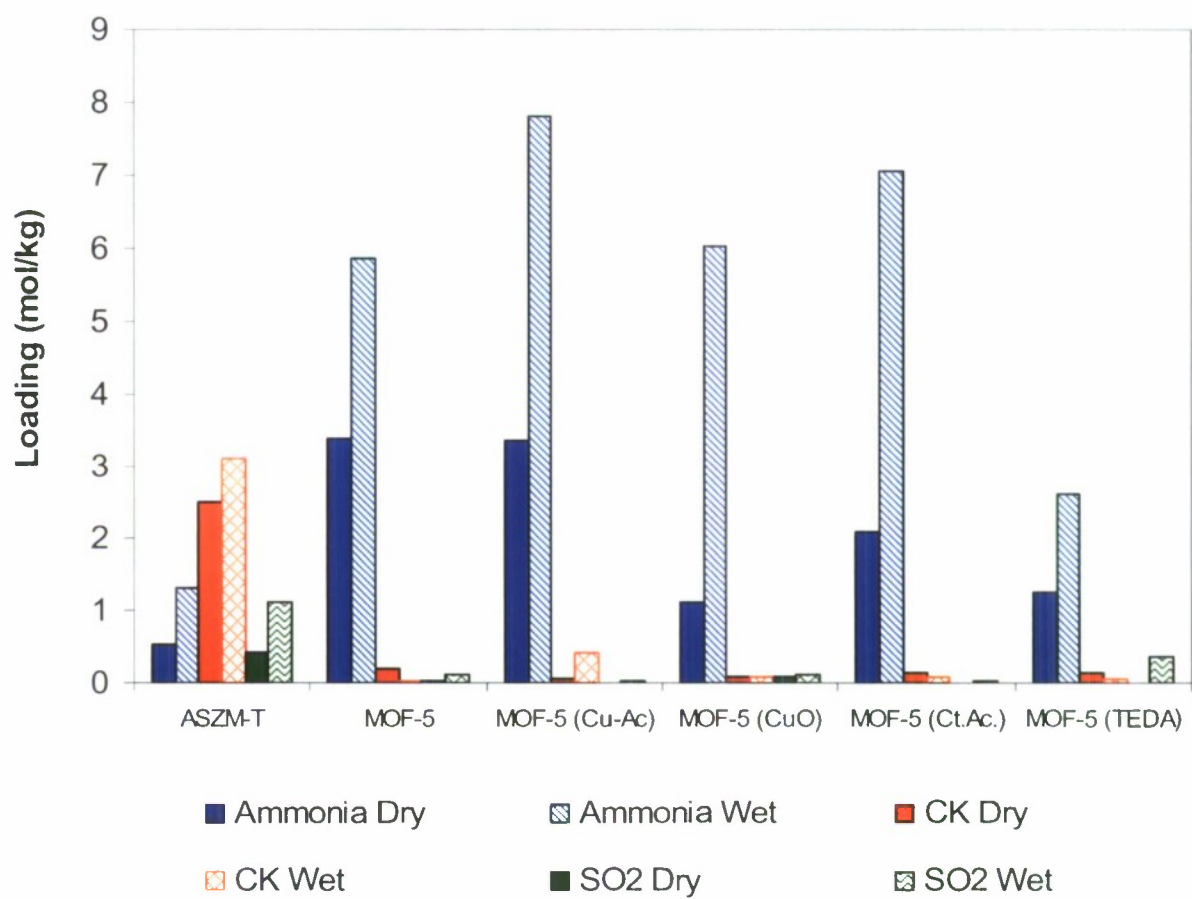


Figure 17. Chemical Removal Summary

Blank

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